

# PATENT COOPERATION TREATY

10/086775  
11-07-03  
Duplex

## PCT

From the INTERNATIONAL SEARCHING AUTHORITY

To:  
EXXONMOBIL RESEARCH AND ENGINEERING  
COMPANY  
Attn. Marin, Mark D.  
P.O.Box 900/1545 Route 22 East  
New Jersey 08801-0900  
UNITED STATES OF AMERICA

RECEIVED

JUN 30 2003

EMRE LAW DEPT.

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference <b>P2002J025</b>	Date of mailing (day/month/year) <b>27/06/2003</b>
International application No. <b>PCT/US 03/03850</b>	International filing date (day/month/year) <b>07/02/2003</b>
Applicant <b>EXXONMOBIL RESEARCH AND ENGINEERING COMPANY</b>	

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

**Filing of amendments and statement under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

**Where?** Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

**For more detailed instructions, see the notes on the accompanying sheet.**

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau.

If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <b>Toñi Muñoz-Manneken</b>
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## NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

### INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

#### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

#### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

#### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

#### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

#### What documents must/may accompany the amendments?

**Letter (Section 205(b)):**

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

## NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

### "Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

### Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

### Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>P2002J025</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/US 03/ 03850</b>	International filing date (day/month/year) <b>07/02/2003</b>	(Earliest) Priority Date (day/month/year) <b>01/03/2002</b>
Applicant  <b>EXXONMOBIL RESEARCH AND ENGINEERING COMPANY</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 5 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☒ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

**LOW EMISSIONS FUEL EMULSION COMPRISING FISCHER-TROPSCH DERIVED HYDROCARBON**

5. With regard to the **abstract**,

the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.

1



None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/03850

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L1/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, FSTA

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 07465 A (REEVES RUSSELL ROBERT ;APACE RES LTD (AU)) 18 February 1999 (1999-02-18) page 6, line 14 - line 18; claims page 10, line 29 -page 11, line 4 ----	1-8, 10-12
X	EP 1 152 049 A (INTEVEP SA) 7 November 2001 (2001-11-07) paragraphs '0015!', '0016!', '0020!', '0032!', '0037!', '0043!', '0143! -----	1-3,9
A	US 6 325 833 B1 (BERLOWITZ PAUL J ET AL) 4 December 2001 (2001-12-04) abstract; claims -----	1-12



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

23 June 2003

Date of mailing of the international search report

27/06/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Bertin-van Bommel, S

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8

A method for reducing particulate emission by combusting an emulsion of fuel and water, said fuel comprising a Fischer-Tropsch derived hydrocarbon with a particle size of 1 micron or less.

2. Claim : 9

A method for forming an emulsion of fuel and water in which the hydrocarbon has a particle size of 1 micron or less, comprising shearing a Fischer-Tropsch derived hydrocarbon and water, in a volume ratio of hydrocarbon to water of from 95:5 to 40:60 and 0.05-5.0 wt% based on the hydrocarbon, and a non-ionic surfactant with an HLB of 5-30.

3. Claims: 10-12

A fuel composition comprising an emulsion of fuel and water, said fuel comprising a Fischer-Tropsch derived hydrocarbon with a particle size of 1 micron or less, said emulsion having a viscosity of above 50 mm/s at 20 degr.C.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 03/03850

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/03850

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9907465	A	18-02-1999	AU 746259 B2	18-04-2002
			AU 8618098 A	01-03-1999
			WO 9907465 A1	18-02-1999
			BR 9811851 A	08-08-2000
			EP 1027143 A1	16-08-2000
			NO 20000540 A	02-02-2000
			US 6444738 B1	03-09-2002
EP 1152049	A	07-11-2001	BR 0101697 A	18-12-2001
			CN 1322793 A	21-11-2001
			EP 1152049 A2	07-11-2001
US 6325833	B1	04-12-2001	AU 734716 B2	21-06-2001
			AU 9385698 A	29-03-1999
			BR 9811783 A	12-09-2000
			CA 2301759 A1	18-03-1999
			DE 69803797 D1	21-03-2002
			DE 69803797 T2	11-07-2002
			DK 1029027 T3	02-04-2002
			EP 1029027 A1	23-08-2000
			ES 2172920 T3	01-10-2002
			JP 2001515950 T	25-09-2001
			NO 20001243 A	08-05-2000
			PT 1029027 T	28-06-2002
			WO 9913031 A1	18-03-1999

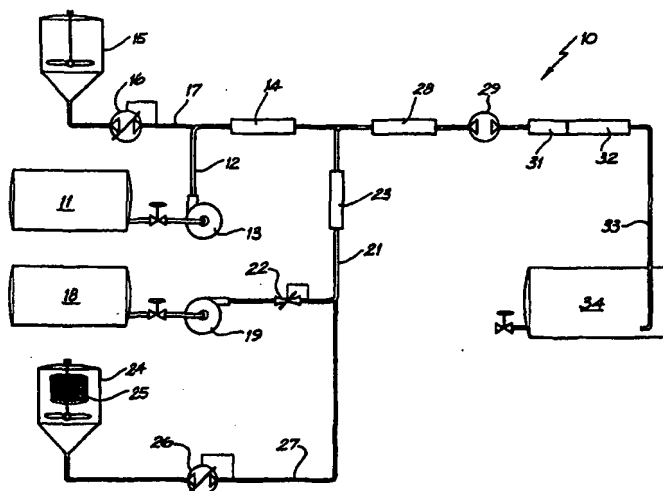




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01F 17/52, C10L 1/18, C08L 53/00		A1	(11) International Publication Number: WO 99/07465
			(43) International Publication Date: 18 February 1999 (18.02.99)
(21) International Application Number: PCT/AU98/00615		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 5 August 1998 (05.08.98)		<p>Published With international search report.</p>	
(30) Priority Data: PO 8411 5 August 1997 (05.08.97) AU			
(71) Applicant (for all designated States except US): APACE RESEARCH LIMITED [AU/AU]; P.O. Box 166, Dungog, NSW 2420 (AU).			
(72) Inventor; and (75) Inventor/Applicant (for US only): REEVES, Russell, Robert [AU/AU]; P.O. Box 166, Dungog, NSW 2420 (AU).			
(74) Agent: F. B. RICE & CO.; 605 Darling Street, Balmain NSW 2041 (AU).			

(54) Title: HEAT STABLE EMULSIONS



(57) Abstract

Emulsions containing a hydrocarbon liquid in a continuous phase and alcohol and/or water in a dispersed phase. The emulsions are stabilised by an emulsifier and a coupling agent. The emulsifier is a copolymer containing at least one relatively hydrophobic polymeric block of styrene or ring substituted styrene monomer, and at least one relatively hydrophilic polymeric block of at least one monomer, such as ethylene oxide, selected from the group having the formula  $H(O-R)_nOH$  where R is an aliphatic radical containing from 1 to 4 carbon atoms and n is a number between 20 and 300. The coupling agent is a copolymer containing at least one polymeric block of styrene or ring substituted styrene monomer, and at least one block being of a saturated or unsaturated aliphatic hydrocarbon moiety, such as butadiene. In order to stabilise the emulsion against stratification or breakage under heat soak conditions the coupling agent contains the styrene monomer and the hydrocarbon moiety in a weight ratio of from 1:0.3 to 1:1.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
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BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
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CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Heat stable emulsionsTechnical Field

The present invention relates to emulsions containing alcohol and/or water in a dispersed phase and a hydrocarbon liquid in the continuous phase. More particularly the present invention relates to such emulsions which are resistant to breaking or stratification of the emulsion under the influence of heat.

Background Art

It is known from the applicant's Australian patent specification 544,728 that emulsions containing alcohol and/or water in one phase and a hydrocarbon liquid in the other may be formed using an emulsifier that is a block copolymer of ethylene oxide and styrene type monomers. These emulsions are of particular utility as liquid transport fuel in which hydrated methanol or hydrated ethanol are dispersed in diesel oil or gasoline. Hydrated alcohol in diesel oil (termed AW/D) emulsions represent a new and potentially cost effective option for significantly reducing particulate and NOx emissions from diesel engines. Emulsions of hydrated alcohol in gasoline exhibit reduced vapour pressure, increased water tolerance and reduced NOx emission on combustion as compared with anhydrous alcohol solutions in gasoline. When the alcohol is ethanol produced from biomass there can be a reduction in the net emission of carbon dioxide ("greenhouse gas") as compared with the use of unblended petroleum fuel.

The arrangement described in the above mentioned specification utilised not only a block copolymer as the emulsifier but also a block copolymer as a coupling agent. The coupling agent typically comprised a block copolymer of butadiene and styrene type monomers. The coupling agents described in that specification contain butadiene and styrene in weight ratios of at least 2:1, more preferably at least 3:1. The emulsifier and the coupling agent are described in that specification as being present in the

emulsion in a ratio of from 1:3 to 3:1. In these ratios solutions of the two copolymers are compatible.

It has been found that while the emulsions described in the aforementioned Australian patent specification produce generally stable emulsions they do suffer from a problem in that the emulsions are not as heat stable as may be desired. This problem is particularly relevant in situations where the emulsions are to be used as fuels. When an engine, particularly a diesel engine, is switched off fuel is left stationary in parts of the engine and fuel supply system that are relatively hot. It has been found that the emulsions disclosed in the aforementioned patent specification are inclined to break or stratify under these "hot soak" conditions. This leaves undispersed alcohol or water in the engine. This can make subsequent starting of the engine difficult, if not impossible, and/or may cause corrosion of the engine.

#### Disclosure of Invention

The present invention relates to an emulsion containing in a continuous phase a hydrocarbon liquid and in a dispersed phase an alcohol and/or water in the presence of:-

(a) an emulsifier being a copolymer containing at least one relatively hydrophobic polymeric block of at least one monomer selected from the group comprising styrene and ring substituted styrenes, and at least one relatively hydrophilic polymeric block of at least one monomer selected from the group having the formula  $H(O-R)_nOH$  where R is an aliphatic radical containing from 1 to 4 carbon atoms and n is a number between 20 and 300, and

(b) a coupling agent being a copolymer containing at least one polymeric block of at least one monomer selected from the group comprising styrene and ring substituted styrenes, and at least one block being a saturated or unsaturated aliphatic hydrocarbon moiety, in which the coupling agent contains the styrene monomer and the

hydrocarbon moiety in a weight ratio of at least 1:1, preferably from 1:0.42 to 1:0.66 depending upon the aromatic content of the hydrocarbon liquid.

The coupling agent is preferably a copolymer containing at least one  
5 polymeric block of at least one monomer selected from the group comprising styrene and ring substituted styrenes and at least one polymeric block of at least one compound selected from the group comprising butadiene or isoprene. Alternatively the hydrocarbon may comprise a single long chain  
10 hydrocarbon moiety rather than a polymer made up of a plurality of recurring monomeric entities. The coupling agent is preferably a pure diblock copolymer or a tapered block copolymer. Such copolymers are preferably produced by anionic solution polymerisation as this technique produces copolymers with a defined structure and a narrow molecular weight  
15 distribution. It is preferred that the coupling agent contains styrene and the aliphatic hydrocarbon in the weight ratio of from 1:0.3 to 1:1, most preferably from 1:0.42 to 1:0.66. As the aromatic content of the continuous phase increases so the preferred ratio of the styrene to the aliphatic hydrocarbon will rise. These ratios are outside the range of at least 1:2 and most preferably 1:3 stated to be desirable in Australian patent specification  
20 544,728 and lead in an opposite direction from the teaching of that specification.

The coupling agent preferably has a molecular weight of from 13,000 to 400,000, more preferably the 100,000 to 170,000, most preferably 120,000 to 150,000. It is preferred that styrene comprises from 50 to 77% by weight  
25 of the coupling agent, most preferably 50 to 70% depending on the aromatic content of the continuous phase of the emulsion. It has been found that when the aromatic content of the continuous phase is less than 22% it is preferable for the styrene content of the coupling agent to be in the range of from 50 to 60% by weight. By contrast when the aromatic content of the

continuous phase is more than 23% it is preferable for the styrene content of the coupling agent to be in the range of from 60 to 70% by weight.

The emulsifier is preferably a copolymer containing at least one polymeric block of at least one monomer selected from the group comprising styrene and ring substituted styrenes and at least one polymeric block of at least one monomer selected from the group having the formula  $H(O-R)_n OH$ , where R is an aliphatic bivalent hydrocarbon radical containing from 1 to 4 carbon atoms and n is a number between 22 and 130. The emulsifier is preferably a pure di-block copolymer or a reaction mixture containing principally di-block copolymer and tri-block copolymer having two blocks of the styrene monomer, together with some unreacted homopolymer of the  $H(O-R)_n OH$  monomer.

In a particularly preferred embodiment of the present invention the emulsifier is a polyethylene oxide-polystyrene copolymer. The polyethylene oxide block is preferably formed first with a molecular weight of between 1,000 and 10,000. The polyethylene oxide and the polystyrene are preferably present in a weight ratio of 1 part of polyethylene oxide to from 0.8 to 1.5 parts of polystyrene, more preferably from 1.0 to 1.25 parts of polystyrene. In preferred embodiments of the invention the emulsifier is produced by the reaction of styrene monomer with polyethylene oxide homopolymer in the presence of a free radical initiator. The reaction product formed without chain transfer agents, comprising polyethylene oxide-polystyrene di-block copolymer, polystyrene-polyethylene oxide-polystyrene tri-block copolymer, unreacted polyethylene oxide homopolymer, and a minor proportion of various other higher molecular weight dimeric and trimeric species and polystyrene homopolymer, is particularly suitable for use in the present invention.

The absolute amounts of the emulsifier and the coupling agent can be determined for any given emulsifier and coupling agent by quantitative testing. It is apparent to the present inventor that the amount of the coupling



agent in the emulsion is important and typically approaches the solubility limit of the coupling agent in the continuous phase. If the amount of the coupling agent is lower than the critical amount it will not couple effectively with the micelles of the emulsifier and therefor stratification of the dispersed phase of the emulsion will not be inhibited. If the amount of the coupling agent is higher than the critical amount it will form micelles of the styrene containing polymeric blocks of the coupling agent which will in turn cause flocculation of the dispersed phase to occur. The solubility of the coupling agent in the continuous phase can be adjusted by an alteration of the amount of the styrene moiety relative to the hydrocarbon moiety in the coupling agent. The solubility will also depend to some extent upon the aromaticity of the hydrocarbon liquid comprising the continuous phase. The more aromatic is the hydrocarbon liquid the higher will be the solubility of any given coupling agent.

The maximum amount of emulsifier is not as critical as the maximum amount of the coupling agent as, within reasonable limits, the presence of an excess of emulsifier has only an economic disadvantage and not a technical one. The emulsifier should be present in an amount greater than 3 times the amount of the coupling agent as is described in more detail later in this specification. Preferred amounts of the coupling agent in the emulsion are in the range of from 0.75 to 1.5 gm/l. When the dispersed phase is hydrated methanol it is preferred that the coupling agent is present in the emulsion in the range of from 0.75 to 1.0 gm/l whereas in the case of the dispersed phase comprising hydrated ethanol the preferred range is from 1.0 to 1.5 gm/l.

In total the copolymer content of the emulsion, i.e. the combined amount of the emulsifier and of the coupling agent, is preferably in the range of from 4 to 10 gm/l. In the case of emulsions containing hydrated methanol in an amount of 12% by volume in the dispersed phase the preferred amount of copolymers is 4 to 6 gm/l, more preferably 5 gm/l, and in the case of emulsions containing hydrated ethanol in an amount of 15% by volume in the

dispersed phase the preferred concentration of copolymers is 5 to 8 gm/l, more preferably 6 gm/l. In the case of emulsions that contain greater amounts of alcohol and/or water in the dispersed phase the preferred amount of the copolymers will typically remain less than 10 gm/l, however in this case the ratio of the emulsifier to the coupling agent will rise. This is because, as the amount of the dispersed phase increases so the quantity of emulsifier required increases in proportion to the increase in the surface area of the dispersed phase of the emulsion; by contrast, the quantity of coupling agent stays substantially constant as the amount of the dispersed phase increases.

As used in this specification the following terms have the meanings indicated:-

Alcohol:

This term means methanol or ethanol or mixtures thereof, and

Hydrocarbon Liquid:

This term includes all liquid fractions obtained from petroleum crude oil and synthetic liquid hydrocarbons obtained from the processing of gaseous or solid hydrocarbons.

The hydrocarbon liquid is preferably selected from the group comprising gasolines, kerosenes, diesel oils, gas oils and fuel oils. The gasolines are liquid hydrocarbons boiling below 190°C. The kerosenes, diesel oils and gas oils boil between 170° and 480°C, while the fuel oils boil above 450°C.

The hydrocarbon liquid is preferably selected from the gasolines, the kerosenes which boil between 170 and 230°C, the diesel oils which boil from 170 to 315°C and the gas oils that boil from 315 to 480°C. The invention is particularly applicable to the high boiling point kerosenes, the diesel oils and the low boiling point gas oils when the dispersed phase comprises a hydrated alcohol. In the case where the dispersed phase comprises only water the

preferred hydrocarbon liquid is selected from the diesel oils, the gas oils, the fuel oils and the hydrocarbon liquids boiling above 480°C.

The dispersed phase of the emulsions preferably comprises a hydrated alcohol, which preferably contains from 0.1 to 10% by volume of water. The dispersed phase is preferably methanol or ethanol, or mixtures thereof, together with water.

The proportions of alcohol and/or water to hydrocarbon liquid may vary over wide limits. For alcohol containing emulsions, a hydrated alcohol content of between 10 and 30% by volume is preferred.

As has been previously described, at the preferred proportions of styrene the solubility of the coupling agent is limited in the continuous phase of the emulsion. This limited solubility encourages coupling of the styrene moieties on the emulsifier with those of the coupling agent thus preventing coalescence of the droplets in the dispersed phase of the emulsion.

It has surprisingly been found that the emulsifier and the coupling agent are desirably included in the emulsion in quite specific amounts. The emulsifier should preferably be present in such an amount that the emulsifier is able to form micelles of its relatively hydrophilic polymer (typically polyethylene oxide) block(s) in a concentration sufficient to contain the alcohol and/or water dispersed phase. The coupling agent should be present in an amount that enables it to couple with, or to form polystyrene micelles only with, the styrene moieties on the emulsifier and to thereby substantially prevent the dispersed phase droplets from coalescing, while not being present in an amount sufficient to form polystyrene micelles of the styrene containing polymeric blocks of the coupling agent itself in the continuous phase of the emulsion. This means that in preferred embodiments of the invention the emulsifier and the coupling agent will be present in a weight ratio of more than 3.0:1, preferably at least 3.5:1, and more preferably at least 4:1. It is surprising that, at these preferred ratios, solutions of the emulsifier

and of the coupling agent are not compatible. These ratios are outside the range of 1:3 to 3:1 stated to be desirable in Australian patent specification 544,728 and lead in an opposite direction from the teaching of that specification.

5           Without being limited to the theory it is suggested that the mechanism of the present emulsification is one of steric stabilisation. It is considered that the emulsifier will form hydrophilic (typically polyethylene oxide) micelles in the continuous phase of the emulsion. The alcohol and/or water is contained within these micelles, the quantity of the alcohol and/or  
10   water that can be accommodated in the emulsion is therefor dependent upon the concentration of these micelles in the emulsion. The styrene block or blocks of the emulsifier have a limited solubility in the continuous phase but will project into the continuous phase from the micelles as their solubility is higher in the continuous phase than in the discontinuous or dispersed phase.

15           The coupling agent has blocks of styrene containing polymer which are only of limited solubility in the continuous phase and a hydrocarbon moiety which is of much greater solubility in the continuous phase of the emulsion. It is believed that the styrene containing polymer blocks of the coupling agent will couple with the corresponding styrene containing  
20   polymer blocks of the emulsifier to form a zone of coupling agent surrounding each micelle. If, however, the amount of coupling agent is increased above a certain concentration, then, as has been discovered by the present inventor, in addition to coupling with the emulsifier the coupling agent molecules will couple with themselves to form polystyrene micelles. If  
25   this happens then rather than acting to maintain a sub-micron dispersion of alcohol and/or water droplets the coupling agent unexpectedly acts to flocculate the dispersed phase, forming comparatively large sized droplets. The presence of the coupling agent is however essential to the maintainance of the sub-micron size dispersion of alcohol and/or water droplets. In the  
30   absence of the coupling agent the micelles of emulsifier flocculate, as the

styrene containing polymer blocks of the emulsifier in adjacent micelles couple together.

The dispersed phase droplets behave in accordance with Stokes Law and may stratify in the emulsion in accordance with the number of droplets, the droplet diameter, the relative density of the dispersed and continuous phases of the emulsion and the viscosity of the continuous phase. The stratification, which is manifest either as creaming, where the dispersed phase rises in the continuous phase, or settling, where the dispersed phase sinks in the continuous phase, may be prevented, or at least reduced, by the establishment of a suitable sub-micron size distribution of the dispersed phase droplets.

It is believed that the emulsifier will form hydrophilic (typically polyethylene oxide) micelles in the continuous phase of the emulsion and, provided the concentration of these micelles is above the necessary minimum concentration for the volume of alcohol and/or water to be incorporated into the emulsion, will contain the alcohol and/or water inside the micelles to form the dispersed phase. It is believed that these initially formed dispersed phase droplets are of a sufficiently small size that they are not susceptible to stratification. It is further believed that if that these initially formed dispersed phase droplets can be prevented from coalescing or agglomerating the emulsion will remain resistant to stratification. If the coupling agent is present in a sufficient amount to couple with the styrene polymer blocks of the emulsifier, but without the formation of micelles of its own, then the initially formed dispersed phase droplets will be held apart and will not be able to couple with one another and coalesce the dispersed phase droplets. The micelles of the emulsifier will thus be stabilised by coupling agent molecules with their styrene polymer blocks coupled to the emulsifier and their hydrocarbon blocks solvated by the continuous phase of the emulsion.

It is postulated that with heat the coupling agent becomes more soluble in the continuous phase of the emulsion. If the hydrocarbon moiety comprises more than 50% by weight of the coupling agent the present inventor has found that the heating of the emulsion can give rise to the coupling agent becoming so soluble in the continuous phase that the styrene polymer blocks will no longer be held in a coupled relationship with the emulsifier. The dispersed phase droplets will then be able to agglomerate. The heat mediated agglomeration of the dispersed phase of the emulsion can lead not just to stratification of the emulsion but to actual breakdown of the emulsion into two distinct phases, one containing substantially only alcohol and/or water and the other substantially only the hydrocarbon liquid.

While the correct selection of the emulsifier and the coupling agent and their relative amounts are important the present inventor has found that a preferred process of forming the emulsion is also desirable. The emulsifier is preferably first dissolved in the alcohol and/or water. In order to induce dissolution of the emulsifier it may be necessary to adjust the reaction conditions used to form the emulsifier to render it more hydrophilic and/or to use an aqueous solution of an alcohol to dissolve the emulsifier. The coupling agent is preferably first dissolved in the hydrocarbon liquid. The alcohol and/or water containing the dissolved emulsifier is then added to the hydrocarbon liquid containing the dissolved coupling agent. It is preferred that the solution of the coupling agent in the hydrocarbon liquid be subjected to agitation both before and after the addition of the alcohol and/or water containing the dissolved emulsifier.

The agitation of the components to the emulsion is preferably carried out using static in-line mixers. In the case of the agitation following the addition of the alcohol and/or water containing the emulsifier to the hydrocarbon liquid containing the dissolved coupling agent it is desirable that the mixing be carried out with high shear. In preferred embodiments of the invention the agitation, combined with the selected emulsifier and

coupling agent, and the use of the process according to the present invention produces emulsions with dispersed droplets having diameters in the range of from 0.1 to 2.0 microns, more preferably from 0.1 to 0.9 microns with an average diameter of about 0.5 microns.

## 5 Brief Description of Drawings

The following description of a preferred embodiment of the present invention is provided as an example of the invention and is described with reference to the accompanying drawings in which:-

- Figure 1 is a flow diagram for a blending facility for forming  
 10 emulsions according to the present invention, and  
 Figure 2 is a graph showing the way in which the percentage stratification of the dispersed phase of an AW/D emulsion changes as the weight percentage of styrene in the coupling agent changes.

## 15 Best Mode for Carrying Out the Invention

### (i) Production of Emulsifier

The following method was used for the production of a 3.27 tonne batch of an emulsifier which is a copolymer of polyethylene oxide and styrene. The method comprised the steps of:-

- 20 a) A suitably sized reactor vessel which is compatible with the emulsifier was cleaned and dried

- b) The following materials were charged into the reactor vessel:-

Polyethylene oxide, molecular weight 1500	804.0 kg
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Xylene solvent	1120.0 kg
----------------	-----------

- 25 The polyethylene oxide had been heated to 50-60°C overnight and was added to the reactor vessel through the manhole.

- |                    |          |
|--------------------|----------|
| c) Styrene monomer | 804.0 kg |
|--------------------|----------|

was charged into the reactor monomer feed headtank.

- |  |          |
|--|----------|
| d) Tertiary butyl perbenzoate free radical initiator | 116.2 kg |
|--|----------|

- |                   |          |
|-------------------|----------|
| 30 Xylene solvent | 426.0 kg |
|-------------------|----------|

were charged into the reactor catalyst feed headtank.

e) A gentle nitrogen flow through the reactor vessel was commenced and the agitator speed set to 40 rpm. The reactor vessel was heated by the application of full heat to the jacket of the reactor vessel.

5 f) When the reactor vessel temperature had reached and levelled out at 140°C the styrene monomer from the reactor monomer feed headtank and the free radical initiator solution from the reactor catalyst headtank were simultaneously fed into the reactor vessel. The feed was continued through rotameters over a period of 12 hours.

10 g) The temperature set point of the reactor vessel was reduced over the 12 hour period of addition from 140°C to 131°C to reduce the severity of reflux. During this period the nitrogen flow was sufficient to blanket the reactor vessel but not so much as to displace refluxing xylene via the condenser catchpot. It was necessary to slow the nitrogen flow as the  
15 volume of the reactor vessel approached capacity during the final 4 hours of the monomer and catalyst feeds.

h) At the completion of the monomer and catalyst feeds the temperature of the product was held constant at approximately 130°C for two hours and agitation of the product was continued during this period.

20 i) The product was then cooled to 100°C. This emulsifier solution had its solids content adjusted to about 50% by weight through the addition of xylene solvent and was then used directly in the production of emulsions. Alternatively, the majority of the xylene may be stripped off by vacuum distillation and recovered for reuse. In this case the reactor contents  
25 would be analysed for solids and the solids content adjusted to about 75% by weight through the addition of hydrated methanol to the reactor.

j) The product was then run-off to drums.

(ii) Production of Coupling Agent.



The preferred coupling agent is produced by a method known as anionic solution polymerisation. This method is widely used in commercial practice for the production of copolymers of styrene and butadiene.

In the conventional anionic solution polymerisation production process, the styrene-butadiene copolymer is usually produced in a solvent of mixed hexanes, then precipitated by the addition of water, dried and sold in solid form. In the present emulsion production application, however, it is preferred to produce the styrene-butadiene copolymer in xylene solvent and to then recover the majority of the xylene solvent and to replace it with the hydrocarbon liquid that is to form the continuous phase of the emulsion. The solids content of the reaction mixture is preferably maintained at about 15% by weight. This coupling agent solution may then be used directly in the production of emulsions.

Alternatively the coupling agent may be prepared by dissolving solid styrene-butadiene copolymer in the manner described in the following steps used to produce a six tonne batch of coupling agent:-

a) A suitably sized reactor vessel which is compatible with the coupling agent was cleaned and dried.

b) The reactor vessel was charged with:-

20	Xylene solvent	2100.0 kg
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c) With the reactor vessel cool the solvent was stirred at 60 rpm. The following was then charged into the reactor vessel through the manhole:-

	Styrene-butadiene copolymer solid crumb	900.0 kg
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d) The manhole cover was sealed and the reactor vessel heated with the jacket temperature initially set at 120°C. As the temperature of the product approached 70°C the jacket temperature was increased to 140° and the stirring rate was increased to 70 rpm.

e) The product was stirred for four hours while maintaining the product temperature below 120°C to avoid degradation of the copolymer. After this period the product was sampled to see that it was clear and free from

undissolved copolymer. The product was then cooled to 100°C and then dropped to an adjustment tank.

f) Additional solvent comprising:-

	xylene solvent	1500.0 kg
5	diesel oil	1500.0 kg

were added to the product in the adjustment tank and the resultant mixture stirred until homogeneous. The product was sampled and the solids content adjusted to 14-15% by weight.

g) The product was then run-off into drums via an in-line filter.

10 (iii) Production of Emulsion.

The blending facility 10 shown in Fig. 1 is designed to blend together diesel oils and alcohol and/or water to form an AW/D emulsion. The emulsion is maintained by the emulsifier and a coupling agent already described.

15 Diesel oil is held in storage tank 11 and is pumped through line 12 by a pump 13 to a first static in-line mixer 14. The coupling agent is a block copolymer of styrene and butadiene dissolved in a reaction solvent, it is stored in a stirred container 15. A metering pump 16 meters the coupling agent through line 17 into the diesel oil conveying line 12 up-stream of the  
20 first static in-line mixer 14. The first static in-line mixer 14 serves to ensure a homogeneous solution of the coupling agent in the diesel oil.

Alcohol and/or water is stored in a tank 18. The alcohol and/or water is pumped from the tank 18 by pump 19 through line 21, including a flow control valve 22, to a second static in-line mixer 23 and then to the line 12  
25 down-stream of the first static in-line mixer 14 and up-stream of a third static in-line mixer 28. The emulsifier is a polyethylene oxide-polystyrene copolymer dissolved in a reaction solvent (or in hydrated alcohol) and is stored in a stirred tank 24 which is maintained at between 35 and 40°C by heating coil 25. The emulsifier is pumped by metering pump 26 along line  
30 27 into line 21, which it enters down-stream of the second mixer 23. The

mixer 23 serves to ensure a homogeneous solution of the emulsifier in the alcohol and/or water. The combined flow of line 12 is then passed through the third static in-line mixer 28.

The homogeneous liquid mixture in line 12 emerging from the third in-line mixer 28 is passed through a fixed displacement pump 29 which has a pressure rise of about 15 bar. The pump 29 conveys the liquid mixture to an in-line static high shear disperser 31 where the emulsion is formed. The emulsion is then passed through a final static in-line mixer 32 and directed through line 33 to a storage tank 34.

If the installation 10 is designed to produce 50 cubic meters per hour of emulsion containing 10% by volume of hydrated ethanol then the pump 13 is operated to pump the diesel oil at approximately 44 cubic meters per hour. The solution of the coupling agent is metered into the diesel at from 0.30 to 0.58 cubic meters per hour by the metering pump 16. The hydrated ethanol flow is controlled by the flow control valve to 5 cubic meters per hour. Metering pump 26 pumps the solution of the emulsifier, as a 50% solids solution in xylene reaction solvent, into the alcohol and/or water at a rate of from 0.42 to 0.48 cubic meters per hour.

(iv) Susceptibility of Emulsions to Heat Mediated Stratification and Breakage.

Emulsions comprising 15% by volume of hydrated alcohol, being the dispersed phase, and diesel oil, being the continuous phase, were tested for stratification. The emulsions were stabilised with an emulsifier comprising a polyethylene oxide-polystyrene copolymer (PEOPS) and a coupling agent comprising a polystyrene-polybutadiene copolymer (PSPB) having a molecular weight in the range from 100,000 to 150,000. In each case the weight of the emulsifier was 8.25 grams/litre of emulsion and the weight of coupling agent was 0.75 grams/litre of emulsion. The weight ratio of the styrene to the butadiene in the coupling agent was varied and the effect of this change correlated with the propensity of the emulsion to stratify.

The propensity of the emulsions to stratify was determined by measuring the percentage of dispersed phase that had stratified or completely separated after 24 hours of undisturbed storage at ambient temperature (10-20°C) following 4 hours storage at 65°C . The results are shown in fig. 2. It  
5 can be seen that the propensity of the emulsions to stratify or break reduces significantly as the weight ratio of styrene in the coupling agent rises above 50%, i.e., as the weight ratio of styrene to butadiene in the coupling agent rises above 1:1.

10 It will be appreciated by persons skilled in the art that numerous changes may be made to the specific embodiments described without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Claims

1. An emulsion containing in a continuous phase a hydrocarbon liquid and in a dispersed phase an alcohol and/or water in the presence of:-

(a) an emulsifier being a copolymer containing at least one relatively hydrophobic polymeric block of at least one monomer selected from the group comprising styrene and ring substituted styrenes, and at least one relatively hydrophilic polymeric block of at least one monomer selected from the group having the formula  $H(O-R)_n OH$  where R is an aliphatic radical containing from 1 to 4 carbon atoms and n is a number between 20 and 300, and

(b) a coupling agent being a copolymer containing at least one polymeric block of at least one monomer selected from the group comprising styrene and ring substituted styrenes, and at least one block being a saturated or unsaturated aliphatic hydrocarbon moiety, the coupling agent contains the styrene monomer and the hydrocarbon moiety in a weight ratio of at least 1:1, preferably from 1:0.3 to 1:1 depending upon the aromatic content of the hydrocarbon liquid.

2. An emulsion as claimed in claim 1, in which the coupling agent contains the styrene monomer and the hydrocarbon moiety in the weight ratio of from

1:0.42 to 1:0.66

3. An emulsion as claimed in claim 1, in which the amount of the coupling agent in the emulsion is in the range of from 0.75 to 1.5 gm/l.

4. An emulsion as claimed in claim 3, in which the dispersed phase contains hydrated methanol and in which the amount of the coupling agent in the

emulsion is in the range of from 0.75 to 1.0 gm/l.

5. An emulsion as claimed in claim 3, in which the dispersed phase contains hydrated ethanol and in which the amount of the coupling agent in the emulsion is in the range of from 1.0 to 1.5 gm/l.

6. An emulsion as claimed in claim 1, in which the total copolymer content of the emulsion is in the range of from 4 to 10 gm/l.
7. An emulsion as claimed in claim 6, in which the dispersed phase contains hydrated methanol and in which the total copolymer content of the emulsion
- 5 is in the range of from 4 to 6 gm/l.
8. An emulsion as claimed in claim 6, in which the dispersed phase contains hydrated ethanol and in which the total copolymer content of the emulsion is in the range of from 5 to 8 gm/l.
9. An emulsion as claimed in claim 1, in which the emulsifier and the
- 10 coupling agent are present in the emulsion in a weight ratio of from greater than 3:1, preferably between 3:1 and 10:1.
10. An emulsion as claimed in claim 9, in which the emulsifier and the coupling agent are present in the emulsion in a weight ratio of from at least 3.5:1, and more preferably at least 4:1.
11. An emulsion as claimed in claim 1, in which the hydrocarbon liquid is selected from the group comprising gasolines, kerosenes, diesel oils, gas oils and fuel oils.
- 15 12. An emulsion as claimed in claim 11, in which the hydrocarbon liquid is a diesel oil.
13. An emulsion as claimed in claim 1, in which the dispersed phase of the emulsion includes alcohol which contains from 0.1 to 10% by volume of water.
- 20 14. An emulsion as claimed in claim 1, in which the dispersed phase of the emulsion contains a hydrated alcohol and comprises between 10 and 30% by volume of the emulsion.
15. An emulsion as claimed in claim 1, in which the emulsifier is a copolymer containing at least one polymeric block of at least one monomer selected from
- 25 the group comprising styrene and ring substituted styrenes and at least one polymeric block of at least one monomer selected from the group having the

formula  $H(O-R)_n OH$ , where R is an aliphatic bivalent hydrocarbon radical containing from 1 to 4 carbon atoms and n is a number between 22 and 130.

16. An emulsion as claimed in claim 1, in which the emulsifier is a pure di-block copolymer or a reaction mixture containing principally di-block copolymer and tri-block copolymer having two blocks of the styrene monomer, together with some unreacted homopolymer of the  $H(O-R)_n OH$  monomer.

17. An emulsion as claimed in claim 1, in which the emulsifier is a polyethylene oxide-polystyrene copolymer.

18. An emulsion as claimed in claim 17, in which the polyethylene oxide block has a molecular weight of between 1,000 and 10,000.

19. An emulsion as claimed in claim 17, in which the polyethylene oxide and the polystyrene are present in a weight ratio of 1 part of polyethylene oxide to from .8 to 1.5 parts of polystyrene, preferably from 1.0 to 1.25 parts of polystyrene.

20. An emulsion as claimed in claim 17, in which the emulsifier is produced by the reaction of styrene monomer with polyethylene oxide homopolymer in the presence of a free radical initiator.

21. An emulsion as claimed in claim 1, in which the coupling agent is a copolymer containing at least one polymeric block of at least one monomer selected from the group comprising styrene and ring substituted styrenes and at least one polymeric block of at least one compound selected from the group butadiene and isoprene.

22. An emulsion as claimed in claim 1, in which the coupling agent is a pure diblock copolymer or a tapered block copolymer.

23. An emulsion as claimed in claim 1, in which the coupling agent has a molecular weight of from 13,000 to 400,000, more preferably the 100,000 to 170,000, most preferably 120,000 to 150,000.

24. An emulsion as claimed in claim 1, in which styrene comprises from 50 to 77% by weight of the coupling agent, most preferably 50 to 70%.

25. An emulsion as claimed in claim 24, in which the aromatic content of the continuous phase is less than 22% and in which styrene comprises from 50 to 60% by weight of the coupling agent.

26. An emulsion as claimed in claim 24, in which the aromatic content of the continuous phase is more than 23% and in which styrene comprises from 60 to 70% by weight of the coupling agent.

27. An emulsion containing in a continuous phase diesel oil and in a dispersed phase a hydrated alcohol in the presence of:-

(a) an emulsifier being a copolymer containing at least one relatively hydrophobic polymeric block of styrene monomer, and at least one relatively hydrophilic polymeric block of ethylene oxide having a molecular weight between 1,000 and 10,000, the polyethylene oxide and the polystyrene being present in a weight ratio of from 1:0.8 to 1:1.5, and

(b) a coupling agent being a copolymer containing at least one polymeric block of styrene monomer and at least one block being polybutadiene, the polystyrene and the polybutadiene being present in a weight ratio of from 1:0.42 to 1:0.66,

the emulsifier being present in an amount sufficient to form micelles of the relatively hydrophilic polymer block sufficient to contain the dispersed

phase and the coupling agent being present in an amount of from 0.75 to 1.5 gm/l, and the emulsifier and the coupling agent being present in the emulsion in a weight ratio of from 3.5:1 to 10:1.



1/2

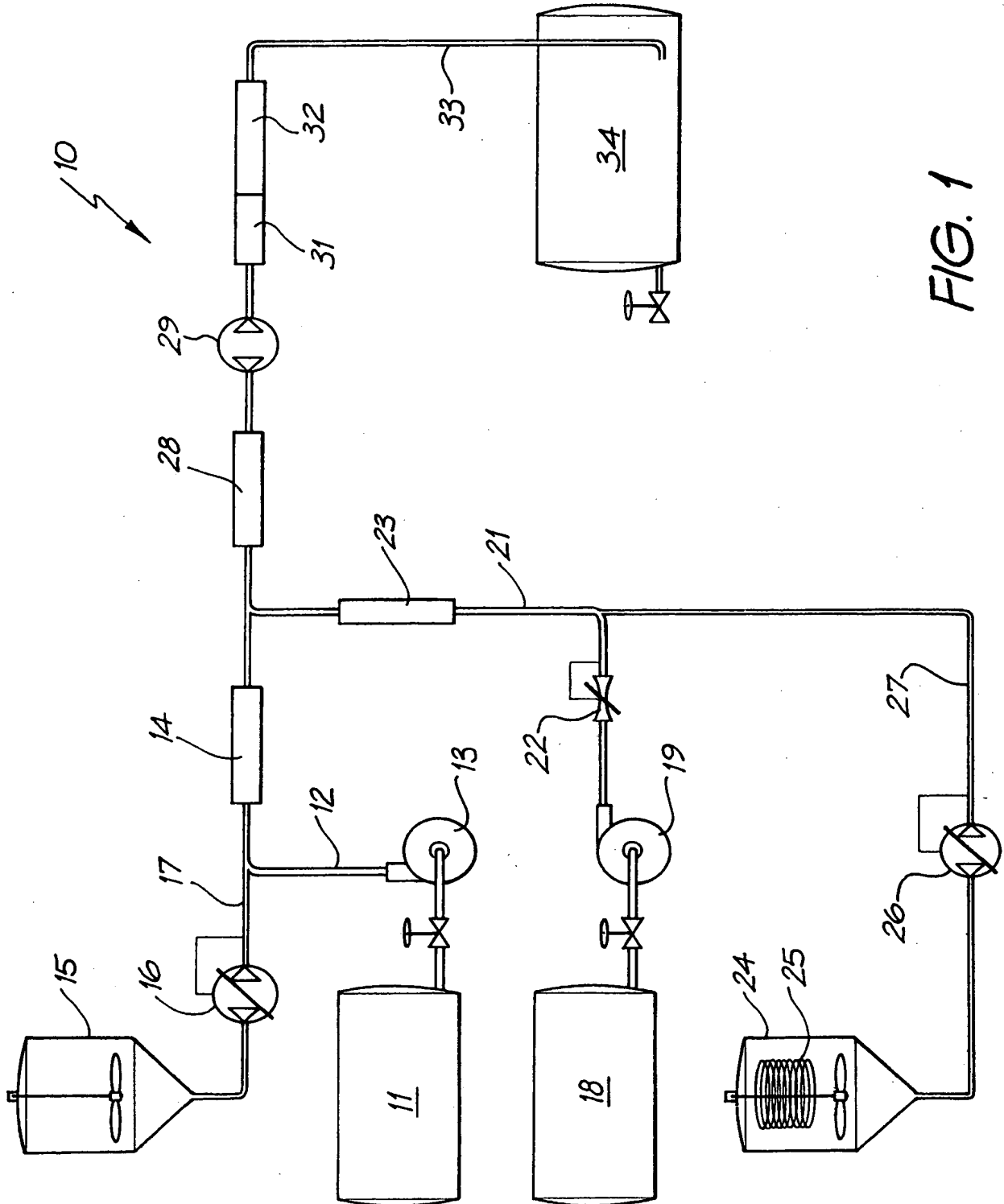


FIG. 1

2/2

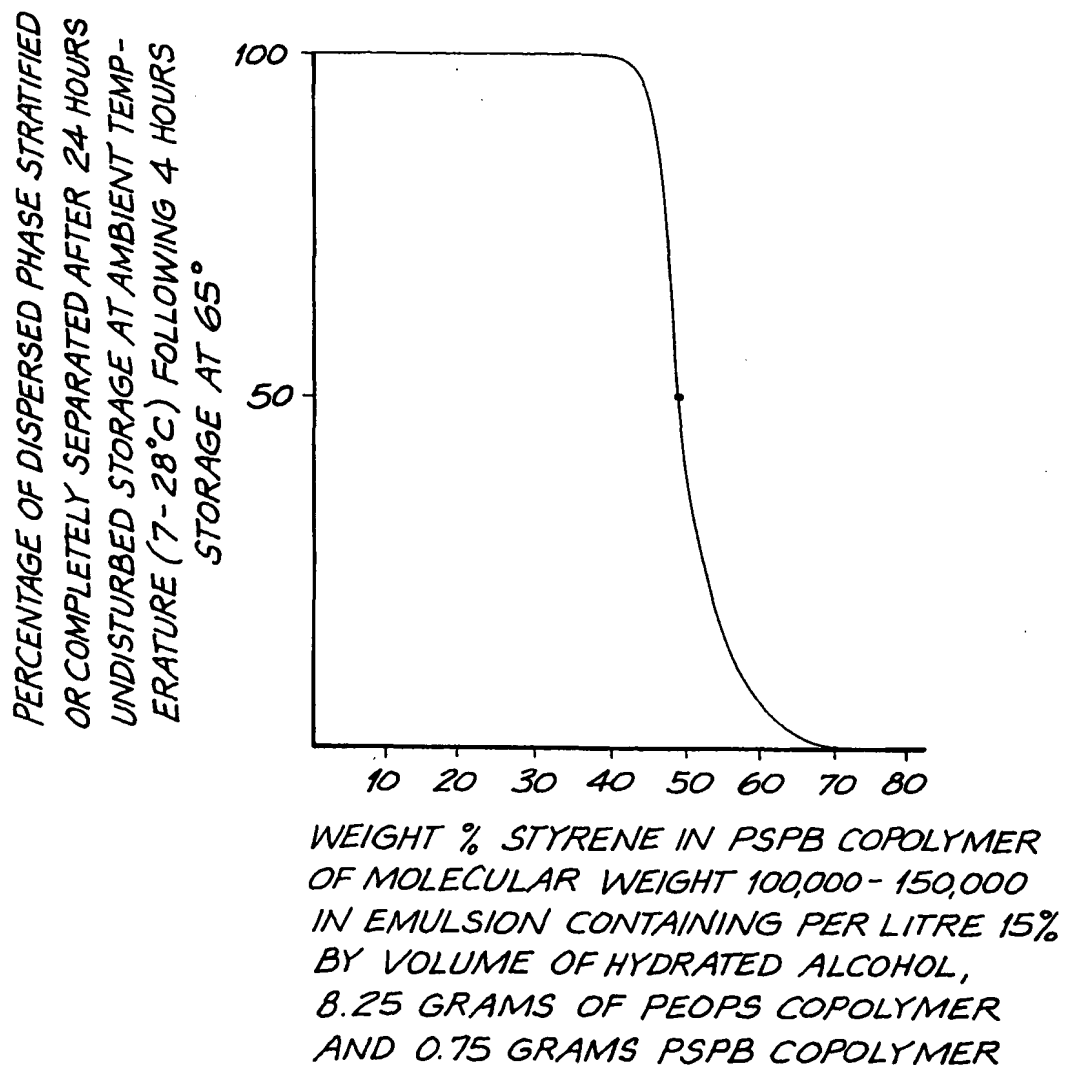
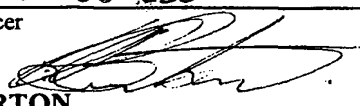


FIG. 2

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/AU 98/00615

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int Cl <sup>6</sup> : B01F 17/52, C10L 1/18, C08L 53/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC B01F 17/52, C10L 1/18		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5484851 (FOCK), 16 January 1996 See whole document	1-27
A	AU B 24141/88 (606760) (ENIRICERCHE S.P.A. et al.) 18 May 1989 See whole document	1-27
A	AU B 12388/83 (544728) (APACE RESEARCH LIMITED et al.) 15 September 1983 See whole document	1-27
<div style="display: flex; justify-content: space-between;"> <span><input type="checkbox"/> Further documents are listed in the continuation of Box C</span> <span><input checked="" type="checkbox"/> See patent family annex</span> </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search 17 August 1998		Date of mailing of the international search report <b>26 AUG 1998</b>
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer  <b>CHRIS BURTON</b> Telephone No.: (02) 6283 2559

## INTERNATIONAL SEARCH REPORT

### Information on patent family members

International Application No.  
**PCT/AU 98/00615**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5484851	EP	5385609	DE	4134967		
AU	24141/88	CA	1327449	FR	2623197	GB	2212162
		JP	1165694	US	4915708		
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